



## **Controlling the Ratio of CZTS to CZTSe Nanocrystals by Hot Injection of Selenium.**

**Engberg, Sara Lena Josefin; Li, Zhenggang; Lam, Yeng Ming; Schou, Jørgen**

*Publication date:*  
2014

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Engberg, S. L. J., Li, Z., Lam, Y. M., & Schou, J. (2014). *Controlling the Ratio of CZTS to CZTSe Nanocrystals by Hot Injection of Selenium..* Poster session presented at 29th European Photovoltaic Solar Energy Conference and Exhibition , Amsterdam, Netherlands.

---

### **General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

# Controlling the Ratio of CZTS to CZTSe Nanocrystals by Hot Injection of Selenium

Sara Engberg<sup>(1)</sup>, Zhenggang Li<sup>(2)</sup>, Jun Yan Lek<sup>(2)</sup>, Yeng Ming Lam<sup>(2)</sup>, Jørgen Schou<sup>(1)</sup>

<sup>(1)</sup>DTU Fotonik, Technical University of Denmark

<sup>(2)</sup>School of Materials Science and Engineering, Nanyang Technological University, Singapore

In this work, we present a wet-chemical method to prepare CZTS and CZTSe nanoparticles in controlled proportions which will result in a film with desired Se content.

## Motivation

We demonstrate precise control in the transformation of CZTS ( $\text{Cu}_2\text{ZnSnS}_4$ ) to CZTSe ( $\text{Cu}_2\text{ZnSnSe}_4$ ) nanoparticles in solution by hot-injection of Se. The proportion of CZTS to CZTSe is determined by the reaction time.

## Method: Synthesizing CZTS and CZTSe Nanocrystals

**Step 1:** CZTS nanocrystals were synthesized using a hot-injection method with oleylamine as the solvent.

**Step 2:** Se dissolved in TOP (trioctylphosphine) was injected into the solution of CZTS, and CZTSe nanocrystals were formed.

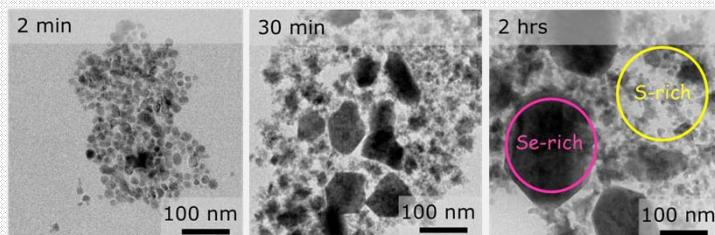


Fig. 1 TEM micrographs of CZTS and CZTSe nanoparticle growth after Se-injection.

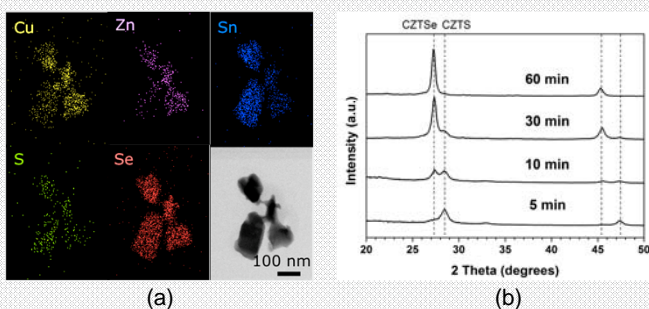
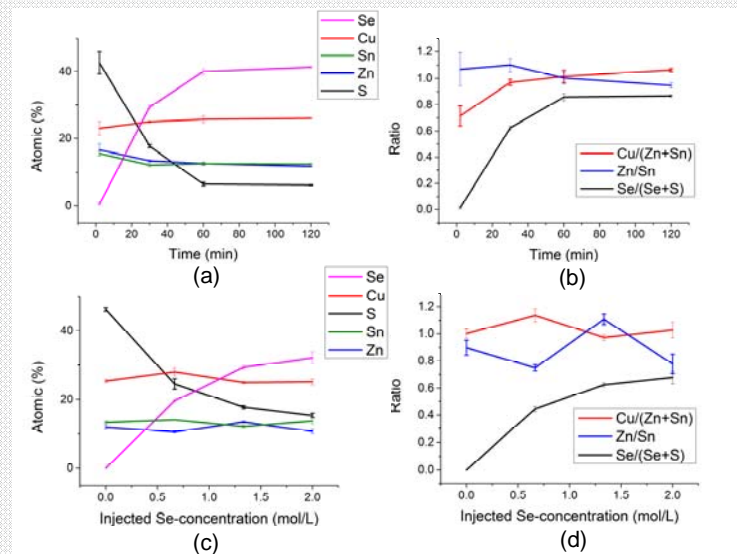


Fig. 2 (a) STEM-EDX elemental mapping of nanocrystals. (b) XRD pattern for CZTS prepared at 220°C for 30 minutes and CZTSe. The diffraction peak positions for CZTS are at 28.48°, 47.43°, and 56.25°. The peaks for CZTSe are at 27.25°, 45.28°, and 53.66°.



Atomic (a) percentages and (b) ratios versus time after Se-injection, at 250°C and 1.33 mol/L Se. Atomic (c) percentages and (d) ratios versus injected Se-concentration, at 250°C after 30 minutes of reaction.

**Particle Size** TEM micrographs of the nanoparticles after Se-injection are shown in Fig. 1. After Se-injection, the largest particle size evolves from approx. 30 nm after 2 min, to 100 nm after 30 min, and finally 200 nm after 2 hours. Notice the presence of a few large and many small nanoparticles at longer times. The large particles were found to be Se-rich, and the small ones S-rich. Additionally, the distinct faceted shapes of the Se-rich particles imply a highly crystalline material.

**Controlled ratios** The reaction rate is fastest in the beginning, and saturates after approx. 1 hour.

**Transformation** STEM-EDX elemental mapping of the nanocrystals, Fig. 2(a), shows evenly distributed atoms. On the contrary, the XRD pattern in Fig. 2(b) indicates that no mixed phase particles are present. The EDX data shows that the ratio of the Se-phase to the S-phase saturates at 80 %, whereas the XRD data indicates 100 % conversion.

## Conclusion

On the basis of the experimental data, we propose that the CZTS nanocrystals decompose into ions as Se is injected. Thus an equilibrium of ions in a solution is formed surrounding the solid nanocrystals, and as Se is injected, a quick nucleation and growth occur to form CZTSe nanocrystals.

## Acknowledgement

This work is financially supported by The Danish Council for Strategic Research.